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EXTRACTIVE METALLURGY OF BERYLLIUM

BY

W. J. KROLL

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EXTRACTIVE METALLURGY OF BERYLLIUM[1]

By W. J. Kroll[2]

INTRODUCTION

The production of beryllium metal and its alloys is one of the most difficult tasks in metallurgy. In this report we shall examine the progress made in this work in the last 15 years, taking into account the outstanding publications, including those of the patent literature, and the information obtained during our 20 years' experience with this metal.

The difficulties experienced in producing elementary beryllium derive from the physical nature as well as from the chemical behavior of the metal and its compounds. Its oxygen affinity is about the same as that of calcium and a little higher than that of magnesium. Its chlorine affinity is much lower than that of magnesium, about equal that of manganese, and little higher than that of aluminum. The sulfur and nitrogen affinity is probably almost the same as that of calcium for these elements, and beryllium carbide is probably more stable than aluminum carbide, Al_4C_3. The intermetallic affinity of beryllium may be given in descending order, as follows: Nickel - copper - iron. It forms eutectics with aluminum and silicon as well as with silver. It does not alloy with magnesium and only partly with calcium. Its oxide melts at 2,570° C., but CaO and BaO form readily fusible eutectics with BeO(65).[3] No igneous solvents are known for BeO, which behaves in this regard like MgO. The beryllium silicate is a strong compound, the aluminate much less so; however, CaO easily displaces BeO in the heated mixtures. The anhydrous chloride hydrolyzes, and it cannot be made from aqueous liquors. It sublimes at 488° C. and melts at 405° C. The fluoride, which is very soluble in water, hydrolyzes also, but a kind of oxyfluoride of the approximate formula 2 BeO·5 BeF_2 can be made from solutions by dessication. The fluoride melts at 800° C. and boils above 1,100° C. It forms very stable double fluorides with alkalifluorides, which have very low melting points and are fairly soluble in water. They are more stable than the analogous fluosilicates and the sodium fluoaluminate cryolite.

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To produce the metal, there are a number of ways that have been used with variable success. They are, essentially, reduction of the chloride, fluoride, or double fluoride with magnesium, calcium, lithium, potassium, or sodium. The electrolytic reduction of these beryllium salts in an inert flux is commonly used. The oxide has been reduced with titanium in a vacuum. Literature mentions the reduction by nascent hydrogen(17) in an arc by low-pressure hydrogen(84), the dissociation of the nitride or carbide, and the electrolysis in liquid ammonia (6, 7) or that of Grignard reagent.

The methods for making alloys are, mainly, the reduction of beryllium halogenides with magnesium, calcium, sodium, lithium, aluminum in the presence of a base metal, or with its alloy with the reducing agent. The fusion electrolysis with a molten-metal cathode has been proposed, as well as the reduction of oxide with calcium or magnesium in the presence of a heavy metal. The reduction of the oxide with carbon in presence of copper or nickel is now common practice.

METHODS FOR PRODUCING THE METAL

Oxide Reduction

Kroll showed(60) that titanium reduces BeO in a high vacuum, and that a high-grade metal can be made in this way. However, the simultaneous volatilization of TiO interferes with the purity of the product. Calcium and magnesium reduce BeO only superficially. These metals can readily be made by the reverse reaction between metallic beryllium and their oxides either at high temperature and atmospheric pressure or at lower temperature in a vacuum.

Carbon reduces BeO at 1,800° C. to Be_2C. The carbide may be dissociated at a still higher temperature(27, 50). As beryllium boils at 2,900° C.(90), the arc must be very hot to carry out the volatilization, and most of the metal vapor may condense on colder carbon parts, where it may recombine. A number of patents refer to this carbon reduction and dissociation (55, 62, 63), and it is common practice of the inventors to include beryllium in any reduction process for magnesium in which carbon is used as reducing agent. However, beryllium is of a very different nature from magnesium, as it forms a stable carbide and is much less volatile. The recovery of beryllium from a carbon-bearing condensate like that obtained in the Hansgirg magnesium process, in which it would be mostly tied up as carbide, is certainly no easy task.

Dissociation methods

If the nitride could be made cheaply, it could, perhaps, be dissociated at high temperature in a vacuum(28, 50). The analogy with aluminum nitride is apparent, as is the possible use of a kind of Serpek process. The beryllium iodide dissociation method(88) was a failure because this compound attacks glass and has too high a dissociation temperature. A number of beryllium alloys, made by the methods described later, could be used for thermal

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dissociation in a vacuum. Zinc(3, 4) and silver-beryllium alloy would be suitable for this purpose. Copper and nickel beryllide, which would be most easily available, are too stable. The boiling points of aluminum, manganese, and silicon are too close to that of beryllium to permit a fair separation from these metals, with which beryllium alloys readily.

Fluoride Reduction

Kroll suggested this method in 1929(57) and used lithium or magnesium as reducing agent. Losano(71) applied this method for making a high-purity metal. The idea was revived by Adamoli(1, 2). The difficulties encountered are these: When using magnesium or lithium as reducing agent, one has to consider the low boiling point of these metals - 1,100° and 1,330° C., respectively. The melting point of beryllium being 1,284° C.(71), the boiling point of the reducing agent is readily reached, owing to the considerable evolution of heat. Calcium, which boils at 1,439° C., develops still more heat, so that it offers no special advantage. One has either to use pressure vessels that withstand the pressure of magnesium vapor at 1,300° C., about 5.5 kg. per cm.^{2} (68 lb. per in.^{2}), which permits obtaining melted beryllium; or one operates with additions that damp the reaction, such as zinc or flux, preferably fluorides. The zinc addition proposed by Cie. Alais-Froges(3, 4) has been adapted by Losano to the reduction of MgF_2 - BeF_2 mixtures with magnesium as reducing agent, as seen from the analysis of the metal, which contains 5 percent Zn(71) and has to be treated at high temperature with a flux to volatilize residual zinc. The reduction at atmospheric pressure, using either fluxes or double fluorides, yields a sintered metal, which has to be remelted. The double fluorides of alkali metals and beryllium are reduced by magnesium with liberation of sodium and beryllium. Since sodium boils at 880° C., only such double fluorides are suitable as contain more than one mol BeF_2 per mol NaF(3, 4, 57) to minimize sodium formation. Additions of CaF_2, MgF_2, SrF_2, BaF_2, and LiF are more favorable, since they are inert against magnesium. Sodium has to be disregarded entirely as a reducing agent for BeF_2(18), because the double fluoride formed cannot be decomposed by sodium beyond $NaF \cdot BeF_2$(18). Difficulties arise also from the crucible question. Losano uses sintered beryllia, but graphite is suitable if impregnated with Be_2C and if the beryllium is not melted by the reaction heat. The difficulties of making pure anhydrous BeF_2 have been overcome by Losano by extraction of the dried aqueous solution with anhydrous alcohol. The poisonous nature of the fluorides forces operation in sealed vessels, and the argon gas seal is advisable.

Chloride Reduction

Given pure oxide-free $BeCl_2$, pure beryllium is easy to make by reduction with Na(34), Li, Ca, or Mg. As a rule, however, the technical chloride is powdery and badly contaminated with oxide. When handled in the air, this fine material picks up more oxide, owing to reaction with moisture, which forms HCl and BeO. The oxide may be present in such large quantities that remelting of the reduced beryllium becomes impossible. Schmidt(85) made, by sodium reduction, a metal with 81 percent Be, by Li reduction with 71 percent Be, the remainder being beryllium oxide. His chloride evidently

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was badly contaminated with BeO, and he worked on too small a scale, which resulted in colloid formation owing to the low temperature of operation. Oxide-free $BeCl_2$ can readily be made, dissolved in a flux, by reaction of solid, comminuted, or molten beryllium copper master alloys of the electric furnace, using molten copper chloride-sodium chloride as a reagent. Closed vessels and gas seal are recommended in this operation. As $BeCl_2$ sublimes at 450° C., inert fluxes are added, which stabilize this salt up to 800° C. by formation of double salts, in which the vapor pressure of $BeCl_2$ is greatly reduced. Mixtures of KCl-NaCl=60-40, which melt at 650° C. and are not hygroscopic, are particularly suitable for this purpose(15). The flux, being generally heavier than the light metals used, would burn during operation in the open air. Therefore, inert-gas protection is recommended(28, 38, 41, 92, 93, 97-99). Hydrogen is suitable for this purpose. The reduction of $BeCl_2$-Mg briquets in hydrogen is described(38, 39, 40, 92).

Metal reductions of chlorides are generally very rapid, and one can reduce completely by using an excess of reagent; however, the main disadvantage of this process, as compared with the fusion electrolysis, is that the crystals have no time to grow and are produced in a very fine form, which may even be attacked by water or form colloid(17). Sodium, when used as reducing agent, has the tendency of forming fine colloidal material(97-99), as described in a French patent(5). Calcium produces coarser metal, but it reacts too violently.

Much attention has been given the use of magnesium as reducing agent. Difficulties have been found in recovering the finely divided metal from the salts. The excess Mg may be removed with NH_4Cl(91), which suggestion was made by Krüss-Morabt(64). Some patents suggest the use of heavy organic liquids to separate oxide or hydroxide from metal, or treatment with weak HNO_3 below 60° C. to extract oxide and other impurities(17, 47). Beryllium bicarbonate dissolution is also proposed(8). In all instances the metal is produced in the solid state, but it has been claimed that the temperature could be raised after the reduction to the melting point of beryllium(97-99). This is evidently a question of a suitable container. As a whole, the magnesium-reduction process looks promising. The fact that $MgCl_2$, LiCl, $CaCl_2$, and $BeCl_2$ are readily soluble in absolute alcohol did apparently escape the attention of the inventors. So is the fact that NaCl, LiCl, KCl, and $MgCl_2$ can easily be removed from the beryllium powder by evaporation in a vacuum at about 900° C. eventually followed by fusion of the beryllium. The possible reuse of the anhydrous $MgCl_2$ for making magnesium is mentioned.

According to a suggestion of Kangro(48), $BeCl_2$ can be reduced at low temperature with aluminum, because $AlCl_3$ is more volatile than $BeCl_2$. Fischer(19) checked this reaction but could not obtain any quantity of beryllium metal, because, as he claims, $BeCl_2$ always contains moisture, which reacts back with the beryllium produced. The present author found that aluminum slightly reduces $BeCl_2$ and that low-grade Be-Al alloys can be made in this way.

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Fusion Electrolysis of the Fluoride

The fusion electrolysis of the sodium-beryllium fluoride, as described by Lebeau(33, 66, 69), has a low efficiency, owing to the fact that with the depletion of the bath a stabler complex is formed, which is higher in NaF and finally yields sodium, as shown by Fischer(18). This could be avoided to some degree by using a bath very rich in BeF_2. Unfortunately, this salt is an insulator that causes a rise in voltage. The solubility of the double fluoride in water is not too good, which makes the reclaiming process for crystals and electrolyte expensive.

The classical Stock-Goldschmidt(42) process deserves only mentioning. It has been abandoned because of the toxicity of the waste gases and the necessity of condensing the fumes to reclaim BeF_2. It may be noticed that the metal made by this method was compact and dense, as it was melted at a contact cathode. The electrolyte was repleted with beryllium oxyfluoride, $2\ BeO \cdot 5\ BeF_2$, which shows that some BeO is decomposed in the cell operation. However, the direct addition of BeO to the fluoride did not work. The solubility of BeO in the fluoride bath used, namely $BaF_2 \cdot BeF_2$, is very low.

The electrolysis of BeO dissolved in cryolite appears frequently in the literature. We found(20) that BeO is indeed soluble in cryolite, as $NaF \cdot BeF_2$ is formed with simultaneous precipitation of Al_2O_3. However, the beryllium-sodium fluoride is a very bad solvent for alumina, and the bath becomes stiff. Aluminum deposits first, and as it reduces BeF_2 slightly, low-grade Al-Be alloy may ultimately be obtained.

Chloride Electrolysis

A stabilizing flux, as described above, is necessary for this operation. The equilibrium diagram $BeCl_2$-NaCl has a minimum at 220° C. and 50 mol percent $BeCl_2$, according to Schmidt(85). Mixtures of KCl-NaCl-LiCl-$BeCl_2$(52, 54) may be electrolyzed at 280° C.; but the addition of LiCl, which is hygroscopic, causes foaming and necessitates reclaiming the salts. Furthermore, the adjustment of a four-salt electrolyte may prove cumbersome. A tungsten anode may be used below 600° C. (35). This is said to show no anode effect. The disadvantages of the fusion electrolysis are the long duration of the operation, which suffers through interference of moisture from the air; the chlorine evolution; the operation in batches; and the necessity of remelting the metal flakes produced, which are unsuitable for most uses. Nothing is won by depleting the bath, as the first crystals always entrap electrolyte, which makes reclamation necessary. The residual $BeCl_2$ is dissolved when the crystals are leached and it can be recovered only as oxide. To avoid a number of these handicaps, some valuable suggestions have been made. Moisture of the air, which produces a milky bath, can be avoided by operation under hydrogen or in an inert gas or in sealed vessels. The electrolyte may be syphoned off after bridging begins(43-45). A very coarse metal is made in this way by the Deutsche Gold und Silber Scheideanstalt. The electrolyte may be repleted after each removal, and the metal crystals may be freed almost completely of $BeCl_2$ by washing with molten flux. The well-described proposition for making smooth layers of metals by fusion electrolysis at low current densities(36) also has been suggested for making Be sheet(83).

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Most beryllium metal is produced today by chloride electrolysis. The necessity of remelting the metal for most uses has been accepted as a fact.

PRODUCTION OF BERYLLIUM ALLOYS

Reduction of BeO With Metals

Time and again it is claimed that beryllium metal can be made by the reduction of the oxide with calcium, magnesium, or aluminum(37, 73). Although this is not correct for making beryllium metal, alloys can be produced in this way. The strong beryllides of nickel, copper, and iron shift the equilibrium considerably in facor of beryllium reduction. We found(58-60) that fine iron powder mixed with $CaCl_2$, BeO, and calcium can be alloyed under argon by reduction of the BeO with 60 percent efficiency calculated on the available Be. Similar results were obtained with copper and calcium, but magnesium gave about half the recovery obtained with calcium. $CaCl_2$ is a good solvent for CaO, but not for MgO. It would not be interesting to operate with readily fusible calcium or barium berylliate slags(65), as the recovery of BeO from such slags would be quite difficult. Pokorny(77) uses Ca-Mg-Fe_2O_3.

Aluminum does not reduce BeO, nor does silicon(58), even when alloyed with iron. However, in presence of BaO the writer was able to reduce BeO with Al, forming an alloy with 0.67 percent Be(59). The claims of Fitzpatrick(21) that high-beryllium alloys can be made in this way are erroneous. Aluminum and silicon-iron alloys did not reduce a trace of beryllium from molten berylliate slags, as the writer found.

Carbon Reduction of BeO to Form Alloys(25)

Lebeau(67, 68) was the first to make beryllium-copper by reduction of BeO with carbon. The writer repeated the experiments in 1932 and found like Lebeau, that separation of metal and residual oxide is difficult. This was uniquely due to the small size of the furnace we used. The writer tried, with success to liquefy the slag by using CaC_2(58, 87), which melts at about 1,600° C., but the metal picked up as much as 1 percent calcium. A CaF_2 flux is recommended by Gruber for treatment of the reduced metal(26).

The reduction of BeO with carbon in the presence of heavy metals or their oxides was put into practice almost simultaneously in this country and in Germany. The Germans used the high-frequency furnace and worked in the beginning either in a vacuum or under hydrogen, apparently to avoid back reaction of the carbon monoxide(30-32, 79-81). Some add metal oxide(53, 75), and others, plain metal(23) in lumps or in powder form. The oxide produces more CO and is cheaper than metal powder, but beryllium losses must be slightly higher, owing to the larger volume of gas. The opinions about the best temperature of operation vary. Some work at 1,285° C.(23), some at 1,900 to 2,300° C.(26), and some at 1,600° C.(53), which seems rather inconsistent. The arc temperature evidently is somewhat different.

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The chemistry of the process can be summarized as follows: Beryllium oxide is reduced to carbide; beryllium carbide reacts with copper, forming beryllide; carbide dissociates, liberating free beryllium according to:

$$2\ BeO + 3C = Be_2C + 2CO,$$

$$3\ Be_2C + 2\ Cu \rightleftarrows 2\ Be_3Cu + 3\ C,$$

$$Be_2C \rightleftarrows 2\ Be + C,$$

$$3\ BeO + 3\ C + Cu = Be_3Cu + 3CO.$$

This latter equation represents a reaction that cannot take place in the arc furnace of the type actually used, as it is lined with carbon, and excess carbon is always present in the reaction zone, so that carbide equilibria prevail. The intermetallic compound rules the equilibrium in proportion to dilution of beryllium by copper. With copper, the equilibrium of the second equation is reached with 4.5 percent Be in the alloy, which is still far from the composition of the compound Be_3Cu containing 29.7 percent Be. With nickel, which forms no carbide but a very strong beryllide, NiBe, the limit composition is about 13 percent Be, which is very close to the theoretical ratio in the compound. The carbon content may be less than 1 percent.

Ferroberyllium cannot be made by reduction with carbon. The writer(58) produced mixtures with 11 percent Be, 13 percent C, and the remainder iron, which disintegrated in air and left iron behind. This was really not iron, but a low-beryllium, low-carbon iron alloy, as can be deduced from the work of Gaev(22, 56), according to which iron with more than 0.5 percent Be produces Be_2C, when heated with carbon. The carbide must be fairly soluble in liquid iron, but it liquates out on cooling. The iron beryllide is evidently much weaker than copper or nickel beryllide, so that the equilibrium reaction between carbide and beryllide proceeds in favor of the former.

Some special items are the subject of patents. It is recommended to use a loose mixture, the density of which should be below 0.4(53). Others use dense material, and copper is added in lumps(23) to collect beryllium vapor above the reaction zone. Some suggest dissolving Be_2C in the metal (79-81) and reacting the bath with BeO, which is a repetition of the old Moissan methods used in a great many analogous cases and even described for refining nickel beryllium(58). Owing to the high temperature and the fineness of the materials charged, flue dust is produced, which has to be collected and recycled. The beryllium losses of the process amount to 10 percent(72). The analogy with the ferrosilicon process regarding volatilization is evident. Some nitride may form, as the furnace is opened temporarily when tapping. The operation in an arc furnace in the absence of a slag is unique, and it is amazing that the materials react despite the fact that the nonmetallic part of the batch is powdery. The melting point of BeO is 2,570° C.; that of Be_2C above 2,100° C., so that if fusion takes place it can be only in the immediate vicinity of the arc. As copper boils at 2,560° C. (90), the reactions in the gas phase must play an important role in the reduction. This process has been the decisive step in making copper-beryllium alloys commercial.

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CHEMICAL METHODS FOR MAKING ALLOYS

Fluoride Reduction. - As fluorides can be reduced to beryllium metal with alkali, alkaline-earth metals, and magnesium, it is evident that alloys can be made in the same way, and even more successfully, if a beryllide can be formed. Advantages result if the reducing agent can be alloyed with the base metal (for example when using magnesium or calcium-nickel or calcium-copper). Alkali metals do not alloy with copper or nickel and may therefore separate from the mixture, come to the bath surface, and burn if no gas seal is provided. The use of alkali metals in the reduction of beryllium fluoride is limited, anyway, by the fact that the complex formed is difficult to split, as shown above (18). Magnesium or its alloys, while suitable for reducing BeF_2, reacts back with NaF, liberating sodium, if the readily fusible double beryllium fluorides are used. Furthermore, the melting diagram, NaF-MgF_2, shows that while there is a minimum at 815° C., there is also a higher melting compound, and, as a whole, the temperature is fairly high. To keep the bath fluid, some BeF_2 must remain behind. This is necessary, also, from the point of view of the elimination of residual magnesium, because the reaction does not proceed to completion. Reclamation of waste salts becomes necessary. Typical examples found in the patent literature are:

$$Mg\text{-}Cu + NaF\cdot BeF_2 (11),$$

$$Li + Ni + BeF_2\cdot NaF (89),$$

$$NaF\cdot BeF_2 + Na + Me (1, 2),$$

$$Mg\text{-}Zn + NaF\cdot BeF_2 (3, 4).$$

This latter proposition, which we verified, shows the difficulties resulting from the absence of beryllide formation, as zinc only dissolves beryllium and forms no compound. The complex cannot be split if too low in BeF_2 and sodium is evolved. Zinc dissolves about 4 percent Be at 800° C., and the metal can be reclaimed by distillation of the zinc from the alloy.

We used quite successfully the reduction of 2 BeO·5 BeF_2 made by evaporation of BeF_2 liquors with magnesium as reducing agent. Briquets are made from magnesium, the above oxyfluoride, and the base-metal powder, or the mixture is compressed into a sheet crucible of the base metal. The furnace, which is of the nichrome resistor type, is contained in a pressure vessel and held under argon during the operation. In the moment of the flash, much gas is evolved, which is permitted to expand through large sections into a rubber balloon. The lining of the crucible is sintered magnesia powder. The metal comes out in ingot form, well-melted. In this way iron, nickel, and copper-beryllium of almost any composition can readily be made with an efficiency of 90 percent on beryllium. With large batches, flux like CaF_2 has to be added, owing to the large amount of heat that is liberated.

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Aluminum reduces BeF_2 to a small extent, and low-grade aluminum-beryllium alloys can be made even with the double fluoride. Magnesium or calcium-aluminum is more effecient, but with the former some magnesium remains in the alloy.

The fluoride reduction for making alloys could be used for obtaining such beryllium alloys, which cannot be made in the arc furnace, like beryllium iron.

Chloride reduction. - As $BeCl_2$ is readily reduced by alkali, alkaline-earth metals, and magnesium, alloys are easy to make in the same way. Beryllide formation favors beryllium reduction. As has been shown for the fluoride reduction, alloys can be used that contain the reducing agent. A number of patents refer to details of the operation. A gas seal has been recognized as important. However this can be avoided, when the mixture is compressed in a crucible made of the base metal in question and submerged in an inert flux(94-96) or submerged in molten base metal(76). The salts may be reduced first, for example, with sodium, and the molten or solid salt-beryllium flux may be poured or put on the molten base metal(94-96). The reduction may even take place with solid powdery reducing alloy, while the salts are melted(16, 39, 78). The base-metal powder also may remain solid(74). These are reactions in the solid phase, in which diffusion plays a major role. Such operations may be important to avoid evaporation losses of $BeCl_2$, as the temperature may be lowered but still be high enough to permit rapid diffusion of the reducing element out of and of beryllium into the base metal. None of these methods has found commercial uses, as it is easier to make copper and nickel beryllium in the arc furnace. However, silver, aluminum(11), iron, and silicon alloys could be made by such methods if there was any demand for them.

Fusion Electrolysis With Metal Cathode

Fluorides and chlorides dissolved in an inert flux have been suggested as bath. Most beryllium alloys have a high melting point, which rather restricts the use of a chloride bath to the electrolysis for making low-grade aluminum alloys. In the Stock-Goldschmidt process, a molten-copper cathode can be used, and the copper may be added as powder(42, 86). Solid deposits can be obrained on copper cathodes(20) as well as on aluminum cathodes(83) when using a very low current density. A number of patents concern the use of two compartment cells to produce metal or alloys by means of an intermediary molten electrode(10, 48).

Alloys Directly From Ore by Carbon Reduction

Beryl ore contains, normally, about 50 percent SiO_2, 10 to 12 percent BeO, and the remainder Al_2O_3. The selective reduction of these impurities has been the subject of some patents. Such methods deserve special attention in view of the treatment of low-grade ores to produce the raw material for chemical processing. In the presence of iron or copper, silicon can be reduced in a first step, but some aluminum enters the alloy if the reduction is pushed to the exhaustion of the silica. This is due to the

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well-known equilibrium between aluminum, silicon, and their oxides. The second plase of the aluminum reduction in the presence of a solvent shows overlapping with the beryllium phase. This leads to alloys containing some beryllium. Aluminum does not reduce beryllia even in presence of iron(58). The contamination with beryllium is due to the back reaction of Be_2C with the base metal. The slag of the second phase necessarily contains carbides; otherwise, aluminum is not removed from the slag. The back reaction of the Be_2C with the base metal has been shown above. With copper as solvent, mixed copper-aluminum-beryllium alloys could be made in the third phase of the process(82). There is no interest in such alloys at present.

Some patents refer to the use of a vacuum or an inert atmosphere(29, 79-81) in the elimination of SiO_2 and production of a high BeO slag for chemical treatment(51), but the main problem of the aluminum-beryllium separation has not been successfully solved.

Among the many suggestions from Gardner, some(24) closely approximate those made by Haglund for the extraction of alumina from clay. When melting beryl with carbon and sulfur-bearing agent, beryllium sulfide is made. Haglund separates silica contained in clay by melting with carbon and pyrite in a hydrogen sulfide atmosphere to produce readily fusible aluminum sulfide (which dissolves alumina) and ferrosilicon. Applied to beryl ore, such a method would permit easy separation of the silica, but mixed beryllium-aluminum sulfides would result.

CONCLUSIONS

The methods for making beryllium metal and its alloys are described and critically analyzed. Titanium reduces the oxide at a high temperature in a good vacuum. The carbon reduction and the dissociation of the carbide, nitride, and iodide are not promising. The fluoride reduction with magnesium yields pure metal. The difficulties resulting from the use of alkali double fluoride are described. In the chloride reduction, the main difficulty is that of obtaining an oxide-free beryllium chloride bath to start with. The metal is precipitated in highly dispersed form, especially when operating on a small scale, and it may react somewhat with water when leaching the cake. A number of patents referring to this technique are discussed. The fusion electrolysis of the fluoride, either according to Lebeau or to Stock-Goldschmidt, has been given up, and the reasons are shown. The chloride electrolysis of beryllium is described in detail. The latest developments appearing in the patent literature are mentioned. Metal of high purity can be made in this way, but it has to be remelted for most uses, as it is obtained as flakes. The major problem is that of producing cheap and oxide-free beryllium chloride. Alloys can be made by reducing BeO with calcium in presence of finely divided base metal using $CaCl_2$ as a flux, but the efficiency is low. The widely used Lebeau process for making copper and nickel beryllium by reduction of BeO with carbon in the presence of these metals or their oxides is examined. It is shown that an equilibrium exists between the beryllium carbide formed and the beryllide in the alloy, which results in the limit of beryllium concentration, namely, 4.5 percent Be in copper and 13 percent in nickel. Iron-beryllium cannot be made by the electric

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arc-furnace method, because any beryllium content above 0.5 percent is tied up as carbide with excess carbon present. Beryllium fluoride can be reduced with magnesium in the presence of a base metal under a gas seal with the formation of alloys. In the same way, using magnesium or sodium, alloys can be made from the beryllium chloride in a flux. Iron beryllium alloys may be made in this way, but there is no need of using such methods for copper or nickel beryllium alloys, which can be made at lower cost in the arc furnace by carbon reduction of the beryllium oxide. The fusion electrolysis with molten-metal cathode is restricted by the melting point of the cathode metal. Low-grade aluminum alloys may be made in this way. The thermal reduction of beryl ore with carbon in the presence of copper or iron is discussed. The elimination of silica in the form of a low-grade ferrosilicon is rather easy, whereas a sharp separation of aluminum and beryllium cannot be obtained. However, such a process, in which the bulk of the silica is eliminated, would be suitable for the beneficiation of low-grade ores if combined with a chemical treatment of the enriched slag.

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BIBLIOGRAPHY

1. ADAMOLI, CARLO. Obtaining Beryllium and Beryllium Alloys. U. S. Patent 2,193,363, March 12, 1940.
2. _____. U. S. Patent 2,193,364, March 12, 1940.
3. ALAIS, FROGES ET CAMARGUE IN PARIS. Preparation of Metallic Beryllium and Its Alloys. British Patent 435,747, Sept. 26, 1935.
4. _____. Verfahren zur Herstellung von Berylliumlegierungen und Metallischen Beryllium. German Patent 675,526, April 21, 1939.
5. ANTIOCH COLLEGE. (Beryllium and Its Compounds.) French Patent 827,315, April 25, 1938.
6. BOOTH, H. S., AND TORREY, GILBERTA G. Electrolysis of Solutions of Beryllium Compounds in Liquid Ammonia. Jorn. Phys. Chem., vol. 35, 1931, pp. 3111-3120.
7. BOOTH, H. S., TORREY, GILBERTA G., AND MENAHEM, MERLUB-SOBEL. Method for the Electrolytic Deposition of Metals. U. S. Patent 1,893,221, Jan. 3, 1933.
8. BUCHER, JOHN E. Recovery of Beryllium. U. S. Patent 2,040,804, May 12, 1936.
9. BURGESS, LOUIS. Manufacture of Beryllium and Beryllium Alloys. U. S. Patent 1,924,151, Aug. 29, 1933.
10. _____. Making Berullium and Light Alloys Thereof. U. S. Patent 1,937,509, Dec. 5, 1933.
11. SOC. AM. PROCESSI PRIVATIVE INDUSTRIALI. (Production of Beryllium Alloys. Italian Patent 342,591, 1936.
12. CLAFLIN, HARRY C. Producing Beryllium Metal. U. S. Patent 1,861,656, June 7, 1932.
13. COOPER, HUGH S. Production of Beryllium. U. S. Patent 1,775,589, Sept. 9, 1930.
14. _____. Production of Beryllium and Other Metals. U. S. Patent 1,805,567, May 19, 1931.
15. _____. Making Beryllium. U. S. Patent 2,076,067, April 6, 1937.
16. _____. Making Alloys. U. S. Patent 2,157,979, May 9, 1939.
17. DOLAN, PAUL M. Method and Apparatus for Reducing Chemicals. U. S. Patent 2,226,525, Dec. 24, 1940.
18. FISCHER, HELLMUT. Beiträge zur analytischen Chemie des Berylliums. Viss. Veroeff. Siemens-Konzern, vol. 8, March 1929, pp. 9-12.
19. FISCHER, HELLMUT, AND PETERS, NEWTON. (Reducibility of Beryllium Chloride with Metallic Aluminum.) Metall u. Erz, vol. 30, 1933, pp. 390-391.
20. FISCHER, H., AND SCHWAN, W. (The Electrodeposition of Beryllium on Copper and Other Metals from a Molten Bath.) Metallwirtschaft, vol. 12, 1933, pp. 187-189.
21. FITZPATRICK, G. D. Beryllium Metal from the Oxide. Chem. Trade Jour., vol. 90, No. 403, 1932, pp. 22-24.
22. GAEV, I. S., AND SOKOLOV, P. S. (Alloys in the Iron-Carbon-Beryllium System.) Metallurg. vol. 12, No. 6, 1937, pp. 11-20. Rev. Instit. Metals, London, vol. 5, 1938, p. 146.
23. GAHAGAN, ANDREW J. Copper-Beryllium Alloys. U. S. Patent 2,193,482, March 12, 1940.
24. GARDNER, DANIEL. Beryllium. British Patent 502,987, March 29, 1939.

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25. GROOM, E. J. Thermal Extraction of Beryllium. Light Metals, London, July 1938, pp. 203-204.
26. GRUBER, HERBERT. Production of Beryllium Copper Alloys. U. S. Patent 2,149,257, March 7, 1939.
27. HERAEUS-VACUUMSCHMELZE AKT. Verfahren zur Herstellung von Beryllium und Berylliumlegierungen. German Patent 635,701, July 28, 1935.
28. _____. Beryllium. German Patent 635,701, Sept. 25, 1936.
29. _____. Beryllium Alloys. German Patent 663,273, Aug. 2, 1938.
30. _____. German Patent Application D. P. a 563,652, July 2, 1930.
31. HERAEUS-VACUUMSCHMELZE, AND ROHN, WILHELM. (Light Metals.) German Patent Application D. P. a. 135,281.
32. _____. Beryllium. German Patent 588,981, Nov. 30, 1933.
33. HOPKINS, B. S., AND MEYER, A. W. The Electrolytic Production of Beryllium. Trans. Electrochem. Soc., vol. 45, 1924, pp. 474-482.
34. HUNTER, M. A., AND JONES, A. The Reduction of Some Rarer Metal Chlorides by Sodium. Trans. Electrochem. Soc., vol. 44, 1933, pp. 23-30.
35. I. G. FARBENINDUSTRIE A. G. (Electrolysis of Fused Halides.) German Patent 514,125, April 27, 1929.
36. _____. Aluminum. German Patent 582,568, Aug. 17, 1933.
37. _____. (Beryllium Alloys.) German Patent 603,051, Sept. 22, 1934.
38. _____. Beryllium. French Patent 819,598, Oct. 21, 1937.
39. _____. Procédé d'obtention d'alliges de beryllium. French Patent 840,490, Jan. 16, 1939.
40. _____. Beryllium. French Patent 837,597, Feb. 14, 1939.
41. _____. (Beryllium Alloys.) German Patent 729,806, No. 26, 1942, add. to German Patent 705,645 (Inventor, H. von Zeppelin)
42. ILLIG, KURT. The Production and Uses of Beryllium. Trans. Electrochem. Soc., vol. 54, 1928, pp. 53-64.
43. JAEGER, GUSTAV. Process for the Preparation of Metallic Beryllium by Electrolysis. U. S. Patent 2,041,131, May 19, 1936.
44. _____. (Producing Metals by Electrolysis.) German Patent 646,088, June 10, 1937.
45. _____. Electrolytic Production of Metals. U. S. Patent 2,151,599, March 21, 1939.
46. _____. Removal of Metallic Magnesium from Mixtures of Beryllium and Magnesium. U. S. Patent 2,274,237, Feb. 24, 1942.
47. JAEGER, G., AND RUDAT, A. (Method of Eliminating Magnesium and Other Impurities from Impure Beryllium.) German Patent 703,517, Nov. 27, 1941.
48. KANGRO, WALTER. (Reducibility of Beryllium Chloride with Metallic Aluminum.) Metall u. Erz, vol. 30, 1933, pp. 389-390.
49. KEELER, LEWIS J. Production of Beryllium Alloys. U. S. Patent 1,790,155, Jan. 27, 1931.
50. KIELLAND, JACOB. Fremgangsmate til fremstilling av beryllium og dets legeringer. Norwegian Patent 55,517, April 12, 1934.
51. KJELLGREN, BENGT R. F., AND SAWYER, C. B. Recovery of Beryllium from Siliceous Ores. U. S. Patent 2,092,621, Sept. 7, 1937.
52. _____. Beryllium. Canadian Patent 371,194, Jan. 11, 1938.
53. _____. Production of Alloys Containing Beryllium. U. S. Patent 2,176,906, Oct. 24, 1939.
54. _____, AND SAWYER, C. B. Producing Metallic Beryllium. U. S. Patent 2,188,904, Feb. 6, 1940.

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55. KJELLGREN, BENGT R. F. Producing Beryllium. U. S. Patent 2,204,221, June 11, 1940.
56. KONTOROVICH, I. E., AND L'VOVSKII, M. Ya. (Cementation of Iron-Carbon Alloys with Beryllium.) Vestnik Metalloprom., vol. 19, No. 12, 1939, pp. 64-70.
57. KROLL, WILHELM. Beryllium. German Patent 480,128, Sept. 29, 1926.
58. _____. (Reducibility of Beryllium Oxide.) Wiss. Veroffeutlich. Siemens Konzern XI, 1932, p. 91.
59. _____. (The Reducibility of the Oxides of the Alkaline Earth Metals, Including Beryllium.) Ztschr. anorg. allgem. Chem., vol. 219, 1934, pp. 301-304.
60. _____. (Reducibility of Beryllium Oxide.) Ztschr. anorg. allgem. Chem., vol. 240, (4), 1939, pp. 332-333.
61. _____. (Anhydrous Fluorides, Properties and Their Uses in Metallurgy). Metall u. Erz., vol. 37, (4), 1940, p. 66.
62. KRUH, OSIAS. Verfahren und Vorrichtung zur Herstellung von Beryllium. Austrian Patent 147,648, June 15, 1936.
63. _____. Production of Beryllium. U. S. Patent 2,121,084, June 21, 1938.
64. KRÜSS, G., AND MORAHT, H. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. J. W. Mellor, vol. IV, 1923, p. 211.
65. LANDOLT-BOERNSTEIN. Physikalisch-chemische Tabellen III, vol. 1, 1935, p. 462, [Photo-Lithoprint Reproduction. 1943].
66. LEBEAU, M. F. Preparation Electrolytique du Glucinium. Ann. chim. phys., vol. 16, ser. 7, 1899, pp. 495-503.
67. _____. Recherches sur le glucinium et ses composés. Ann chim. phys., vol. 16, S. 7, 1899, pp. 457-503.
68. LEBEAU, M. P. Sur la preparation des alliages de glucinium. Alliages de glucinium et de cuivre. Compt. rend., vol, 125, 1897, pp. 1172-1174.
69. _____. Preparation du glucinium par électrolyse. Compt. rend., vol. 126, 1898, pp. 744-746.
70. LIEMPT, J. A. M. VAN. (Electrodeposition of Tungsten (from Fused Electrolytes).) Ztschr. Elektrochem., vol. 31, 1925, p. 252.
71. LOSANO, L. (Properties of Very Pure Beryllium.) Alluminio, vol. 8, No. 2, 1939, pp. 67-75.
72. MANTELL, C. L. Electrolytic Production of Beryllium Alloys. Industrial Electrochemistry, 2d ed., McGraw-Hill Book Co., New York, 1940, p. 436.
73. MERCK, E. Darstellung von Berylliummetall. German Patent 410,563, Dec. 21, 1923.
74. MERLUB-SOBEL, MENAHEM. Producing Beryllium Alloys. U. S. Patent 2,135,983, Nov. 8, 1938.
75. NISCHK, KURT. (Studies on Double Decompositions between Metals or Metal Oxides and Carbon.) Ztschr. Elektrochem., vol. 29, 1923, pp. 373-390.
76. POKORNY, ERNST. Obtaining Heavy-Metal Beryllium Alloys. U. S. Patent 1,949,082, Feb. 27, 1934.
77. POKORNY, ERNST, AND SCHNEIDER, K. Producing Heavy-Metal-Beryllium Alloys. U. S. Patent 1,945,565, Feb. 6, 1934.
78. RICHARDSON, HAROLD A. Alloys. British Patent 520,643, April 30, 1940.
79. ROHN, WILHELM. Producing Beryllium Alloys. U. S. Patent 2,025,614, Dec. 24, 1935.

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80. ROHN, WILHELM. U. S. Patent 2,025,615, Dec. 24, 1935.
81. _____. U. S. Patent 2,025,616, Dec. 24, 1935, German Patent 663,305, 1937.
82. _____, AND GRUBER, HERBERT. (Beryllium and Its Alloys.) German Patent 732,128, Jan. 28, 1943.
83. SAWYER, CHARLES B., AND KJELLGREN, R. F. Electrolytic Production of Beryllium Sheets. U. S. Patent 2,311,257, Feb. 16, 1945.
84. SCHLECHT, HELMUT, AND JOHRSTORFER, M. Reduction of Difficultly Reducible Oxides. U. S. Patent 2,242,759, May 20, 1941.
85. SCHMIDT, J. M. (Study of Beryllium and Its Chloride.) Ann. Chem., vol. 11, 1929, p. 352.
86. SIEMENS AND HALSKE, A. G. (Beryllium Alloys.) German Patent 486,452, Nov. 14, 1928.
87. _____, AND KROLL, WILHELM. (Beryllium Alloys.) German Patent 626,402, Feb. 26, 1936.
88. SLOMAN, H. A. Researches on Beryllium. Jour. Inst. Metals, vol. 49, (2), 1932, pp. 377-378.
89. SOCIETA ANOMINA PROCESSI PRIVATIVE INDUSTRIALI. Italian Patent 342,591, Aug. 10, 1936.
90. VAN ARKEL, A. E. Reine Metalle. Herstellung-Eigenschaften-Verwendung. Berlin. J. Springer, 1939, appendix.
91. VON ZEPPELIN, HELMUT. Treating Metal Mixtures. U. S. Patent 2,170,394, Aug. 22, 1939.
92. _____. Production of Reguline Beryllium and Beryllium Alloys. U. S. Patent 2,171,439, Aug. 29, 1939.
93. _____. Beryllium. German Patent 705,645, March 27, 1941. (See Reference 42.)
94. _____. Beryllium. U. S. Patent 2,250,087, July 29, 1941.
95. _____. Production of Alloys Containing Beryllium. U. S. Patent 2,251,088, July 29, 1941.
96. _____. Production of Alloys Containing Beryllium. U. S. Patent 2,251,089, July 29, 1941.
97. WEMPE, BERNHARD. Beryllium Alloys. British Patent 428,458, May 8, 1935.
98. _____. Production of Pure Beryllium. U. S. Patent 2,091,087, Aug. 24, 1937.
99. _____. (Pure Reguline Beryllium.) German Patent 719,031, March 5, 1942.

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